ARMY RESEARCH LABORATORY

Externally Activated Surface Modification Using Diels-Alder Ligand Chemistry and Selective Immiscibility

by Frederick L. Beyer, Philip J. Costanzo, and John D. Demaree

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory

Aberdeen Proving Ground, MD 21005-5069

Externally Activated Surface Modification
Using Diels-Alder Ligand Chemistry
and Selective Immiscibility

Frederick L. Beyer, Philip J. Costanzo, and John D. Demaree
Weapons and Materials Research Directorate, ARL

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
March 2007	Final	August 2005–August 2006

4. TITLE AND SUBTITLE

Externally Activated Surface Modification Using Diels-Alder Ligand Chemistry and Selective Immiscibility

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Frederick L. Beyer, Philip J. Costanzo, and John D. Demaree

5d. PROJECT NUMBER

AH42

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Research Laboratory
ATTN: AMSRD-ARL-WM-MA
Aberdeen Proving Ground, MD 21005-5069

8. PERFORMING ORGANIZATION REPORT NUMBER

ARL-TN-271

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Gold particles 10 nm in diameter have been uniformly dispersed using a new dispersing agent (ligand) that is a diblock copolymer containing a Diels-Alder linkage between the blocks. Heating the sample to a specified temperature causes the particles to migrate to the surface of the film. This new strategy could be used to create coatings that can be deliberately activated or modified using an external trigger.

15. SUBJECT TERMS

nanoparticle, TEM, SAXS, USAXS, gold ligand, block copolymer

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UNCLASSIFIED	**b. ABSTRACT** UNCLASSIFIED	**c. THIS PAGE** UNCLASSIFIED	UL	18	Frederick L. Beyer
					19b. TELEPHONE NUMBER (*Include area code*) 410-306-0893

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Contents

List of Figures

Acknowledgments

INTENTIONALLY LEFT BLANK.

1. Introduction

Controlling the chemistry of a polymer surface is relevant to a broad range of U.S. Army systems in a wide range of environments. An example of an unmet need for functional surfaces and coatings might be as simple as a vehicle coating with an embedded ability to self-decontaminate, particularly if the decontamination process could be remotely activated via an external variable (temperature, light, magnetic field, etc.). In this example, following an exposure to a chemical or biological weapon, the coating functionality could be activated by exposing the vehicle to the appropriate condition, rendering it safe to the occupants and ready for use. Other military applications include selective identification uses, antifouling, or possibly even selective alteration of mechanical properties in specific areas.

Polymer surface functionalization has been approached in several different ways, including creating surfaces that are inhomogeneous or patterned or functionalizing portions of specific molecules so that they "bloom" to the surface of a film (*1–3*). These techniques are versatile and can be very effective depending on the circumstance and strategy employed, but they have limitations that include scalability and longevity.

The premise of the current research project is illustrated in figure 1. The inherent characteristic of thermodynamic immiscibility of most polymers (*4*) will be combined with the facile chemistry of the Diels-Alder reaction to create a dispersing agent (or ligand) that can be easily changed by simply elevating temperature. A Diels-Alder reaction will be used to join two highly immiscible polymers to create a linear diblock copolymer ligand. The blocks of the ligand will be chosen so when tethered to a nanoscopic particle, the outer block will be miscible with the polymer matrix into which the particles are to be mixed. Once dispersed, the reversibility of the Diels-Alder linkage will be used to break apart the ligand, exposing the other block of the copolymer ligand. Because that block has been specifically chosen to be strongly immiscible with the matrix material, this will render the particles themselves immiscible in the polymer matrix, creating a driving force for phase separation to the nearest surface or area of high concentration of particles.

2. Experimental

A detailed description of the experimental procedures used in this work will soon be available; a synopsis will be given here (*5*).

Poly(ethylene glycol) (PEG) was chosen as the outer portion of the diblock copolymer ligand, while poly(styrene) (PS) was chosen to be the inner portion. A maleimide was added to commercially available PEG, while reversible addition fragmentation transfer polymerization
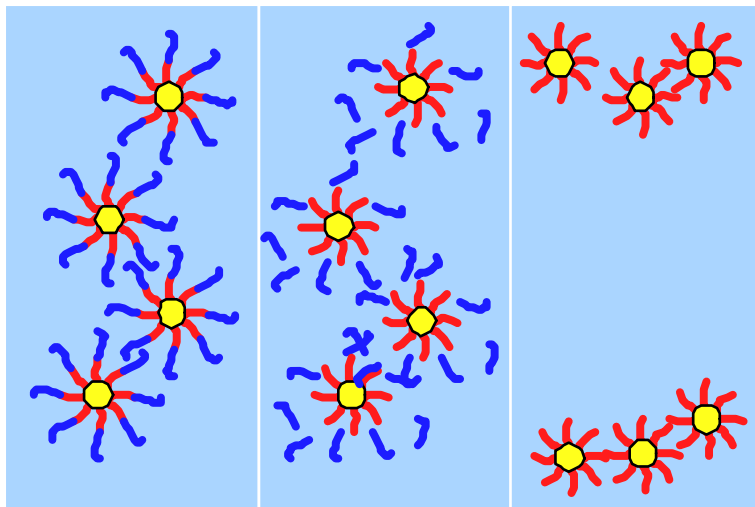
Figure 1. Schematic illustrating the effect of incorporating the Diels-Alder moiety into the compatibilizing ligand for a nanoparticle additive. From left to right, dispersed particles with block copolymer ligands, dispersed but immiscible particles immediately after dissociation of the Diels-Alder bond, and immiscible particles after migration.

was used to make the PS block and address the need for a furyl-functionalized PS. The PS block was also functionalized with a thiol so it could be attached to the gold nanoparticles. The two blocks were then reacted together at 60 °C for several days, forming the block copolymer ligand.

Gold particles were fabricated using a standard procedure (*6*). Small-angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) were used to measure particle size, which was found to be on average 10 nm in diameter. TEM data were collected using a JEOL 200CX instrument operated at 120-kV accelerating voltage.

The gold particles were functionalized with the diblock copolymer ligand by dispersing the particles and dissolving the ligand in toluene and stirring for several hours. Bulk samples were then fabricated by creating solutions of commercially available 2000 g/mol PEG homopolymer and the functionalized gold nanoparticles and allowing the solvent to evaporate, leaving bulk films ~500 µm thick. Because the Diels-Alder adduct used here is favored at temperatures below 60 °C and the separate products are favored at temperatures above 90 °C, the critical change in morphology was induced by annealing the samples for various times at 90 °C under vacuum.

The surfaces of the samples were characterized using contact angle and Rutherford backscattering (RBS) measurements. RBS experiments were performed using 1.2-MeV He+ ion beams from an NEC 5SDH-2 tandem positive ion accelerator. The backscattering angle was 170°, and the solid angle of the surface barrier detector was approximately 4 millisteradians. All spectra were fit and interpreted using the program RUMP (*7*). Contact angles were recorded

with image capture software written in LabVIEW and a charge-coupled-device camera. High-performance liquid chromatography-grade water was used, and individual measurements were made by outlining the drop with an arc and then recording the tangent angle formed at the substrate surface. The bulk morphology of the samples were characterized using ultrasmall-angle x-ray scattering (USAXS). USAXS data were collected at the UNICAT beam line 33ID at the Advanced Photon Source (Argonne National Laboratory, Argonne, Illinois) (*8*). All data are given as intensity I as a function of scattering angle q, where $q = (4\pi/\lambda) \cdot \sin(\theta)$, where λ is the wavelength and θ is 1/2 the scattering angle.

3. Results

Figure 2 shows a TEM micrograph of the ligand-functionalized nanoparticles when drop-cast from solution onto a TEM grid. It was not possible to obtain TEM data for the bulk samples because of the waxy nature of the PEG matrices used in this study. The molecular weight of the PEG matrix used here (2000 g/mol) is substantially below the entanglement molecular weight of PEG, which makes TEM sample preparation difficult. However, changes in the visual appearance of the samples indicated that, when annealed, the samples underwent a bulk morphological transformation.
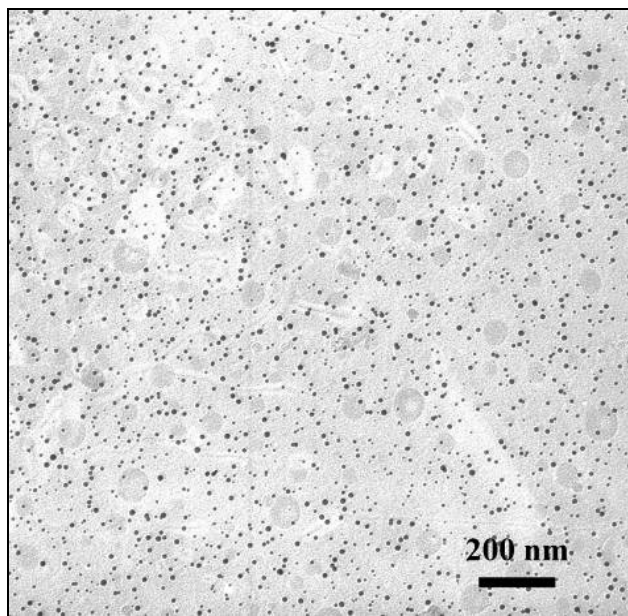

Figure 2. A TEM micrograph of diblock copolymer-functionalized gold nanoparticles after being dropcast directly onto a TEM grid (no PEG matrix). The addition of the copolymer ligand results in a uniform dispersion.

This implication was confirmed by USAXS, for which data are shown in figure 3. The USAXS data span two angular regimes of interest: the very lowest angles ($0.0001 < q < 0.01$) and the more traditional small-angle regime ($0.01 < q < 0.2$). In the small-angle regime, a Guinier "knee" is apparent. This feature is due to intraparticle scattering from the gold/ligand particle additives (*9*). This feature, from ligand-modified gold particles, was fit using a log-normal particle size distribution and the form factor for a solid sphere, giving the mean particle size of 10 nm reported earlier. The lack of any evidence of a deviation from the linear regimes at very low angles supports the assertion that the particles are well dispersed in the PEG matrix (*10*).
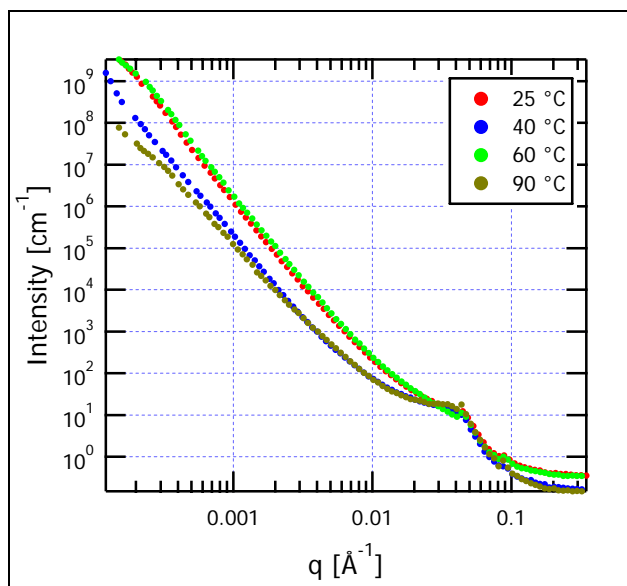

Figure 3. USAXS data showing no upturn at very low angles (large length scales), indicating that the gold nanoparticles are well-dispersed in the bulk PEG matrices before and after annealing.

Figure 4 shows contact angle measurements of a sample having the same composite composition after being annealed for various times at 90 °C. Anneal results in a clear increase in the contact angle of water on the surface. The initial contact angle measurement is approximately that of pure PEG. When the sample is annealed, the contact angle gradually changes, approaching that of PS. This indicates that the composition of the sample surface is changing, which is attributed to migration of particles to the surface. This migration would only be the result of a change in the miscibility of the dispersed particles, the result of the separation of the Diels-Alder linkage when the temperature of the sample reaches 90 °C.
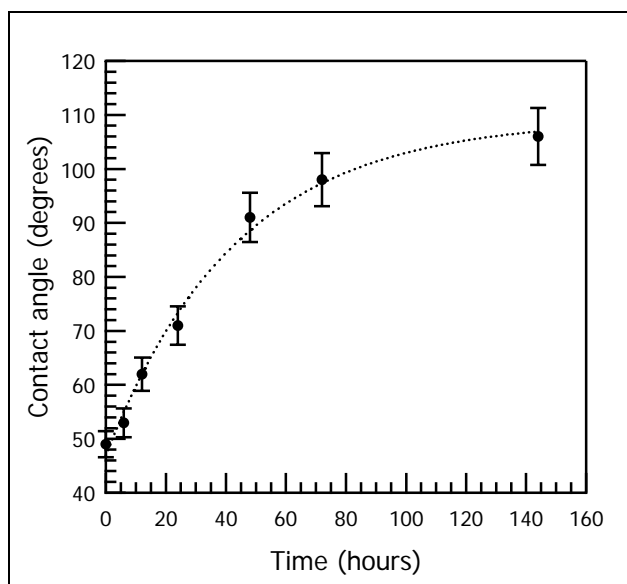
Figure 4. Contact angle data showing the increase in
contact angle with annealing time, a result of
increasing migration of the PS component of
the block copolymer ligand to the surface of the
bulk material. The dotted curve is an
exponential function fit to the data and should
only be taken as a visual guide.

The RBS data shown in figure 5 clearly support this interpretation and confirm the migration of gold to the sample surface. The data recorded in the highest energy channels (farthest to the right) result from the presence of high atomic number atoms (here, gold) within 2 µm of the sample surface. Annealing the samples for longer periods of time at 90 °C causes the appearance of a peak at the surface, indicating that breaking the Diels-Alder adduct does result in a nonequilibrium condition within the material that drives the gold nanoparticles to the surface of the film. Moreover, this change in surface character is not observed in control experiments where the block copolymer is formed with a temperature stable linkage between the PS and PEG. This clearly shows that severing the Diels-Alder linkage is the fundamental step that results in a change in the morphology of these materials in the bulk.

4.   Conclusions

Here it has been shown that by incorporating a Diels-Alder linkage into a diblock copolymer ligand, one can control the miscibility of a particulate additive in a low molecular weight polymer matrix. By heating the samples to 90 °C, where the Diels-Alder linkage is not favored, the particles can be converted from being miscible to being immiscible. This results in a strong driving force for the particles to move away from the matrix. This driving force is satisfied by

Figure 5. RBS data for a 2000 g/mol PEG matrix containing 4 weight-percent gold nanoparticle/block copolymer ligand additive. The increase with time of the peak between channels 400 and 450 indicates the migration of the gold particles to the film surface.

the accumulation of the particles at the sample surfaces. Migration of the particles was determined by contact angle measurements and RBS experiments. The dispersed nature of the samples before and after annealing was indicated by USAXS measurements.

5. References

1. Diehl, K. A.; Foley, J. D.; Nealey, P. F.; Murphy, C. J. Nanoscale Topography Modulates Corneal Epithelial Cell Migration. *Journal of Biomedical Materials Research Part A* **2005**, *75A*, 603–611.

2. Genzer, J. Templating Surfaces With Gradient Assemblies. *Journal of Adhesion* **2005**, *81*, 417–435.

3. Mason, R.; Jalbert, C. A.; Muisener, P.; Koberstein, J. T.; Elman, J. F.; Long, T. E.; Gunesin, B. Z. Surface Energy and Surface Composition of End-Fluorinated Polystyrene. *Advances in Colloid and Interface Science* **2001**, *94*, 1–19.

4. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

5. Costanzo, P. J.; Demaree, J. D.; Beyer, F. L. Controlling Dispersion and Migration of Particulate Additives with Block Copolymers and Diels-Alder Chemistry. Langmuir, accepted for publication*,* 2006.

6. Hiramatsu, H.; Osterloh, F. E. A Simple Large-Scale Synthesis of Nearly Monodisperse Gold and Silver Nanoparticles With Adjustable Sizes and With Exchangeable Surfactants. *Chemistry of Materials* **2004**, *16*, 2509–2511.

7. Doolittle, L. R. A Semiautomatic Algorithm for Rutherford Backscattering Analysis. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms* **1986**, *15*, 227–231.

8. Long, G. G.; Allen, A. J.; Ilavsky, J.; Jemian, P. R.; Zschack, P. The Ultra-Small-Angle X-ray Scattering Instrument on UNICAT at the APS. *SRI99: Eleventh U.S. National Synchrotron Radiation Instrumentation Conference*, Stanford, CA, 13–15 October 1999; American Institute of Physics: Melville, NY, 2000, 183–187.

9. Roe, R.-J. *Methods of X-ray and Neutron Scattering in Polymer Science*; Oxford University Press: New York, NY, 2000.

10. Kammler, H. K.; Beaucage, G.; Mueller, R.; Pratsinis, S. E. Structure of Flame-Made Silica Nanoparticles by Ultra-Small-Angle X-Ray Scattering. *Langmuir* **2004**, *20*, 1915–1921.

NO. OF
COPIES   ORGANIZATION

  1   DEFENSE TECHNICAL
(PDF   INFORMATION CTR
ONLY)   DTIC OCA
         8725 JOHN J KINGMAN RD
         STE 0944
         FORT BELVOIR VA 22060-6218

  1   US ARMY RSRCH DEV &
         ENGRG CMD
         SYSTEMS OF SYSTEMS
         INTEGRATION
         AMSRD SS T
         6000 6TH ST STE 100
         FORT BELVOIR VA 22060-5608

  1   DIRECTOR
         US ARMY RESEARCH LAB
         IMNE ALC IMS
         2800 POWDER MILL RD
         ADELPHI MD 20783-1197

  3   DIRECTOR
         US ARMY RESEARCH LAB
         AMSRD ARL CI OK TL
         2800 POWDER MILL RD
         ADELPHI MD 20783-1197

         ABERDEEN PROVING GROUND

  1   DIR USARL
         AMSRD ARL CI OK TP (BLDG 4600)

NO. OF
<u>COPIES</u> <u>ORGANIZATION</u>

<u>ABERDEEN PROVING GROUND</u>

6   DIR USARL
     AMSRD ARL WM MA
     F BEYER (2 CPS)
     P COSTANZO (2 CPS)
     J DEMAREE (2 CPS)

INTENTIONALLY LEFT BLANK.